

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

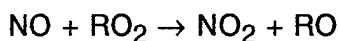
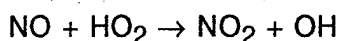
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1997	3. REPORT TYPE AND DATES COVERED From Proceeding of 1997 Workshop	
4. TITLE AND SUBTITLE Effect of Hydrocarbons on Plasma Treatment of NOx			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) B.M. Penetrante, W.J. Pitz, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Lawrence Livermore National Laboratory Livermore, CA 94550			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES This work was performed under the auspices of the US Department of Energy under contract number W-7405-ENG-48. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner. From Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 Words) This paper examines how hydrocarbons affect the non-thermal plasma treatment of NOx in lean-aburn engine exhausts.				
14. SUBJECT TERMS NOx; NO2; hydrocarbons; lean-burn; SERDP; SERDP Collection			15. NUMBER OF PAGES 5	
			16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT unclass.	18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.	20. LIMITATION OF ABSTRACT UL	

EFFECT OF HYDROCARBONS ON PLASMA TREATMENT OF NO_x

B. M. Penetrante, W. J. Pitz, M. C. Hsiao, B. T. Merritt and G. E. Vogtlin

Lawrence Livermore National Laboratory, Livermore, CA 94550

Abstract: This paper examines how hydrocarbons affect the non-thermal plasma treatment of NO_x in lean-burn engine exhausts. We have found that the NO is mainly oxidized to NO₂ by



where R is a hydrocarbon radical. The O and OH radicals produced by electron-impact dissociation are consumed mainly by reactions with the hydrocarbons rather than with NO. The hydrocarbons lower the energy cost for the oxidation of NO by converting O and OH to HO₂; the OH radical is then reproduced when NO is oxidized by HO₂. This cyclic process leads to a very efficient utilization of the plasma-produced radicals for the selective partial oxidation of NO to NO₂. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N₂ can only be accomplished through heterogeneous reactions of NO₂ with surfaces or particulates.

I. Introduction

Lean-burn gasoline engine exhausts contain a significant amount of hydrocarbons in the form of propene. Diesel engine exhausts contain little gaseous hydrocarbon; however, they contain a significant amount of liquid-phase hydrocarbons (known as the volatile organic fraction) in the particulates.

The objective of this paper is to examine the fate of NO_x when an exhaust gas mixture that contains hydrocarbons is subjected to a plasma. We will show that the hydrocarbons promote the oxidation of NO to NO₂, but not the reduction of

NO to N₂. The oxidation of NO to NO₂ is strongly coupled with the hydrocarbon oxidation chemistry. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N₂ can only be accomplished through heterogeneous reactions of NO₂ with surfaces or particulates.

II. Test Setup

Previous studies [1-3] have shown that all electrical discharge plasma reactors produce a plasma with an average electron kinetic energy of around 3-6 eV. The plasma chemistry in discharge plasma reactors is therefore very similar regardless of electrode structure or the way the voltage is delivered to the reactor.

The plasma reactor used in this study is a pulsed corona consisting of a 1.5 mm diameter wire in a 60 mm diameter metal tube 300 mm long. Heater bands and thermocouples provide active control of the processor temperature. The power supply is a magnetic pulse compression system capable of delivering up to 30 kV output into 100 ns pulses at variable repetition rates to the kilohertz range. The electrical energy deposition into the gas was determined by monitoring the electrical parameters associated with the discharge.

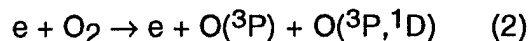
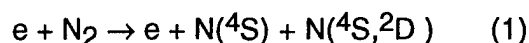
The experiments were performed in a flow-through configuration. We prepared a mixture containing trace amounts of NO and hydrocarbons and recorded the composition of the effluent gas as a function of input electrical energy density. The input energy density, Joules per standard liter (J/L), is the ratio of discharge power to gas flow rate at standard conditions (25°C and 1 atm). The gas blending manifold allowed us to custom make gas streams consisting of N₂, O₂, propene and

NO_x. We metered these gases through mass flow controllers which permitted exact control of flow rate. We used calibrated gas mixtures of either hydrocarbons or NO in N₂. This arrangement allowed us to blend in small concentrations of the trace components using mass flow controllers. After mixing in the manifold, the gas then passed through a temperature controlled heater which preheated the gas to the processor temperature. We monitored the outlet gas composition with a Fourier Transform Infrared (FTIR) spectrometer. We heated the absorption cell to 120°C to avoid condensation of any water byproduct.

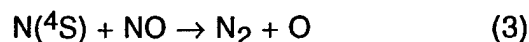
III. Plasma Process Without Hydrocarbons

Lean-burn engine exhausts contain high concentrations of oxygen, rendering conventional catalytic converters ineffective for the treatment of NO_x. A critical issue in the application of plasma-based methods to cars and trucks is whether the NO is removed by reduction to benign gases such as N₂, or by oxidation to NO₂ and nitric acid. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction to N₂.

Oxidation is the dominant process for exhausts containing dilute concentrations of NO in mixtures of N₂, O₂ and H₂O, particularly when the O₂ concentration is 5% or higher. The kinetic energy of the electrons is deposited primarily into the major gas components, N₂ and O₂. The most useful deposition of energy is associated with the production of N and O radicals through electron-impact dissociation:

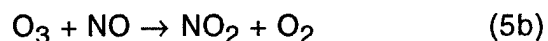
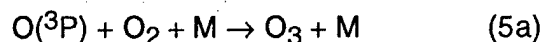
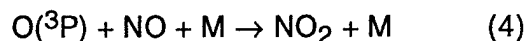


where N(^4S) and N(^2D) are ground-state and metastable excited-state nitrogen atoms, respectively, and O(^3P) (simply referred to as O) and O(^1D) are ground-state and metastable excited-state oxygen atoms, respectively. The N(^4S) is the only plasma-produced species that could lead to the chemical reduction of NO:

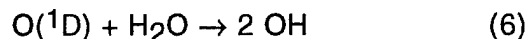


In the presence of O₂, the oxidation pathway becomes dominant for two reasons:

(a) The dissociation energy of O₂ is smaller than that of N₂. For electrical discharge plasma reactors, the average electron kinetic energy is low, around 3-6 eV.[1-3] Under this condition the rate for dissociation of O₂ is much higher compared to the dissociation of N₂. [4] The dissociation of O₂ will produce only oxidative radicals. The ground-state oxygen atom, O(^3P), will convert NO to NO₂ via

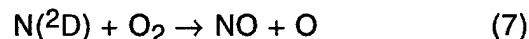


The metastable oxygen atom, O(^1D), will react with H₂O to produce OH radicals:



The OH radicals will convert NO and NO₂ to nitrous and nitric acid, respectively.

(b) Under conditions optimum for the dissociation of N₂, the production of the reducing species, N(^4S), also leads to the production of the metastable atomic nitrogen, N(^2D). [5] The N(^2D) species can lead to undesired reactions in the presence of O₂. Rather than reducing NO, the N(^2D) species would react with O₂ to produce NO:



The production of NO by N(^2D) will counterbalance the reduction of NO by N(^4S), thus effectively leaving oxidation as the only pathway for NO conversion.

We examined the plasma processing of 100 ppm NO in 10% O₂ and balance N₂, without hydrocarbons. The NO_x concentrations for the cases at 100°C and 300°C are shown in Figures 1(a) and 1(b), respectively. They are plotted as a function of electrical energy density (J/L). For the 100°C case, about 60% of the NO is converted to NO₂ at energy densities of 40 J/L and above. For the 300°C case, the conversion of NO to NO₂ is

only around 20% even at the high energy densities.

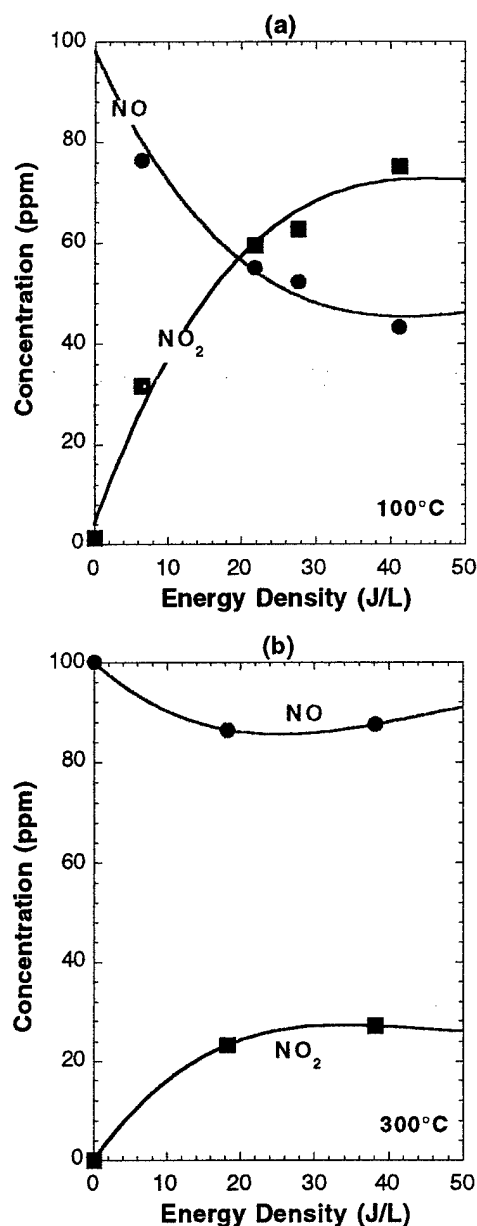
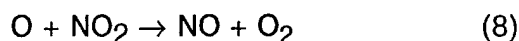


Figure 1. Effect of temperature on the plasma oxidation of NO in the absence of hydrocarbons. Plasma processing of 100 ppm NO in 10% O₂, balance N₂, at (a) 100°C and (b) 300°C.

The efficiency for oxidation of NO to NO₂ drops as the temperature is increased. At high temperatures, the NO to NO₂ oxidation reactions are counteracted by the reduction reaction:



Without hydrocarbons the oxidation of NO by the O radical is not efficient at high temperatures.

IV. Plasma Process With Hydrocarbons

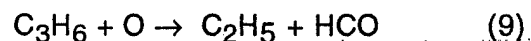
We next examined the effect of hydrocarbons on the plasma processing of NO. Propene was used as a representative hydrocarbon. The gas mixture contained 500 ppm NO in 10% O₂ and balance N₂. The NO_x concentrations for the cases without propene and with 1000 ppm propene are shown in Figures 2(a) and 2(b), respectively, for processing at 300°C. For the case without propene (Figure 2(a)), less than 20% of the NO is converted to NO₂ even at the high energy densities. This is consistent with the previous observation shown in Figure 1(b). At high temperatures, the efficiency for conversion of NO to NO₂ is poor in the absence of hydrocarbons in the gas stream. Figure 2(b) shows the NO_x concentrations when 1000 ppm of propene is added to this gas stream. The main fate of NO in the plasma in the presence of hydrocarbons is the oxidation of NO to NO₂.

The oxidation of NO to NO₂ is coupled with the hydrocarbon oxidation chemistry and will be discussed in the following section.

V. Oxidation Chemistry

This section will discuss the hydrocarbon oxidation chemistry, using propene as the representative hydrocarbon.

In the very early stages of reaction the propene is mainly consumed by the O atom:



Of the total reaction with O atom, reaction (9) contributes 50%, and reactions (10) and (11) contribute 25% each. The O atoms are consumed more effectively by reactions (9)-(11) than reactions (4) and (5): $\text{O} + \text{NO} \rightarrow \text{NO}_2$.

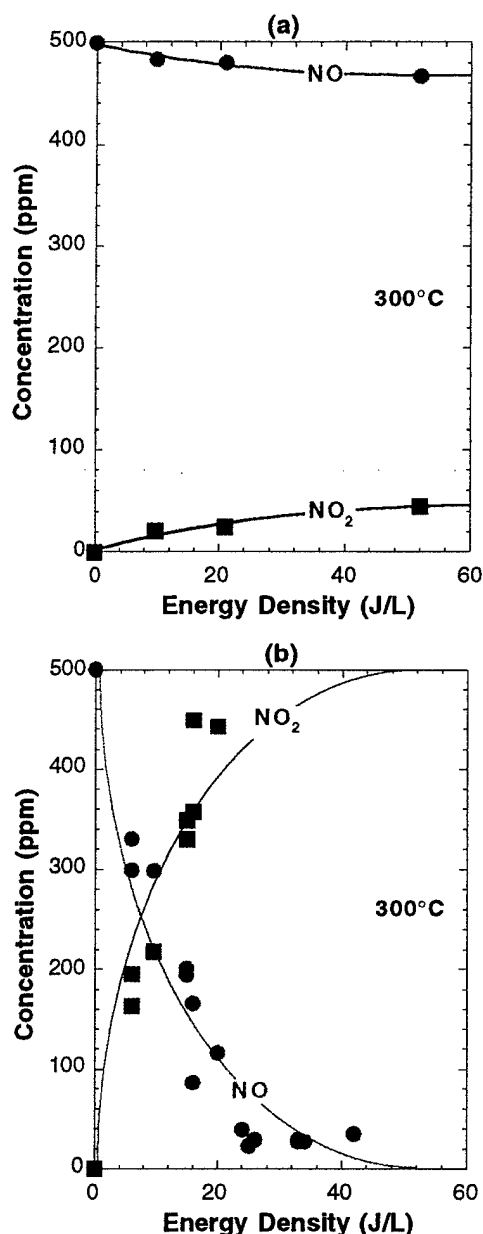
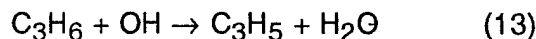
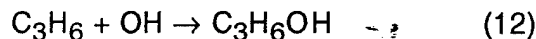


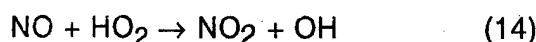
Figure 2. Effect of propene on the plasma oxidation of NO at 300°C. Plasma processing of 500 ppm NO in 10% O₂, balance N₂, (a) without propene, and (b) with 1000 ppm propene.

At 300°C and early in the reaction, about 98% of the O atoms react with propene compared to 2% with NO. The rate constants for propene + O are much faster than that of NO + O. This result means that the propene consumes most of the O atoms that might otherwise react with NO to form NO₂.

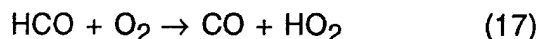
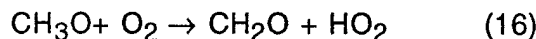
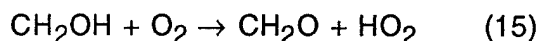
After the initial stages of reaction, the OH radical rather than O atom becomes the main radical consuming propene:



where C₃H₅ radical symbolized all three isomers, which were distinguished individually in the reaction mechanism. The switch from O atom reactions to OH reactions is mainly due to OH being produced by the reaction



This is also the main reaction that converts NO to NO₂. The HO₂ radicals are also produced from reactions involving hydrocarbon intermediates of propene oxidation:



Therefore, the propene supplies HO₂ radicals which convert NO to NO₂. Without the propene, the main reaction to convert NO to NO₂ are reactions (4) and (5): O + NO → NO₂.

Nearly all the O atoms for conversion are supplied by electron impact, which has an associated cost in electrical energy. The propene lowers the energy requirement by production of HO₂ radicals which then become the main radical for conversion of NO to NO₂.

The OH produced from reaction (6) can also react with NO and NO₂ to form their related acids:

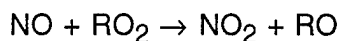
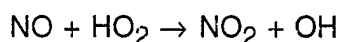


At 300°C, during the time when the propene is being consumed most rapidly, only about 6% of the OH is reacting with NO and NO₂ while the remainder is reacting mostly with propene and its aldehydic intermediate products. At 100°C, 15% of the OH is reacting with NO and NO₂, while the remainder reacting mostly with propene and

aldehydic intermediates. The rate constants for these reactions are much slower than for propene + OH reactions, so that OH reacts mainly with propene rather than NO and NO₂.

VI. Conclusions

The objective of this paper was to examine the fate of NO when a lean-burn exhaust gas that contains hydrocarbons is subjected to a non-thermal plasma. We have found that the NO is mainly oxidized to NO₂ by



where R is a hydrocarbon radical. The oxidation of NO to NO₂ is coupled with the hydrocarbon oxidation chemistry. The O and OH radicals are consumed mainly by reactions with the hydrocarbons rather than with NO. Only oxidizing radicals in the form of HO₂ and RO₂ are produced during the breakup of the hydrocarbons. The hydrocarbons lower the energy cost for the oxidation of NO by converting O and OH to HO₂; the OH radical is then reproduced when NO is oxidized by HO₂. This cyclic process leads to a very efficient utilization of the plasma-produced radicals for the selective partial oxidation of NO to NO₂. This result suggests that gas-phase reactions in the plasma alone cannot lead to the chemical reduction of NO_x. Any reduction of NO_x to N₂ can only be accomplished through heterogeneous reactions of NO₂ with surfaces or particulates.

VII. Acknowledgments

This work was performed at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the Office of Basic Energy Sciences and a Cooperative Research and Development Agreement with Cummins Engine Company.

VIII. References

- [1] B.M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin, P.H. Wallman, M. Neiger, O. Wolf, T. Hammer and S. Broer: *Applied Physics Letters* **68** (1996) 3719.
- [2] B.M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin, P.H. Wallman, A. Kuthi, C.P. Burkhardt and J.R. Bayless: *Applied Physics Letters* **67** (1995) 3096.
- [3] B. M. Penetrante, M.C. Hsiao, B.T. Merritt, G.E. Vogtlin and P.H. Wallman, *IEEE Transactions on Plasma Science* **23** (1995) 679.
- [4] B.M. Penetrante, in *Non-Thermal Plasma Techniques for Pollution Control - Part A: Overview, Fundamentals and Supporting Technologies*, edited by B. M. Penetrante and S. E. Schultheis (Springer-Verlag, Berlin Heidelberg New York, 1993) pp. 65-90.
- [5] B.M. Penetrante, J.N. Bardsley and M.C. Hsiao, *Japanese Journal of Applied Physics* **36** (1997) 5007.